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Dr. Richard S. Miller

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COMPUTATIONAL INVESTIGATION OF THE STABILITIES OF SOME N, O, F IONS

by

M. Edward Grice and Peter Politzer

Department of Chemistry
University of New Orleans
New Orleans, LA 70148

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13. ABSTRACT (Maximum 200 words)

In response to the suggestion of Jeff Bottaro (SRI International), we have investigated the potential stabilities of four N, O, F ions, **1** - **4**.

All four molecular geometries were optimized using a non-local density functional (DF) procedure (Gaussian 92/DFT; BLYP/6-31+G**) and also at the *ab initio* MP2/6-31+G** (frozen core) level. For **1**, the MP optimization was carried out as well without the frozen-core approximation. All calculations were for spin-restricted singlet states; however the DF results were checked for stability relative to allowing them to become spin-unrestricted and/or complex and were determined to be stable in this respect.

In order to ascertain whether the optimized structures correspond to true energy minima, vibration frequencies were computed for all four systems at the DF level and for **1** and **2** at the MP2; for the anions **3** and **4**, the number of basis functions being used precluded MP2 frequency calculations. No imaginary vibration frequencies were found. This confirms that the optimized structures of all four systems do correspond to true energy minima, and that these ions should be able to exist.

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The computed energies and geometries are shown below. Energies are in hartrees (1 hartree = 627.5 kcal/mole), distances in Å and angles in degrees. For the most part, the geometries obtained by the two procedures are very similar.

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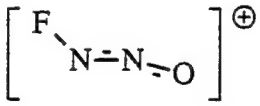
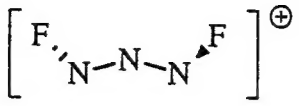
1 

Both DF and MP2 optimizations gave a planar C_S structure.

	DF	MP2-FC	MP2
Energy	-283.99968	-283.30446	-283.31763
F-N	1.343	1.335	1.333
N-N	1.216	1.208	1.204
O-N	1.164	1.155	1.155
F-N-N	121.80	126.96	126.51
O-N-N	157.98	157.91	158.28

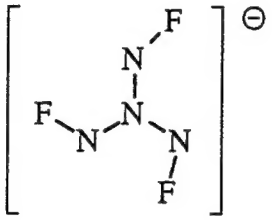
2



Both optimizations gave a C_2 structure with bent N-N-N and the fluorines out of the N-N-N plane.

	DF	MP2-FC
Energy	-363.33081	-362.43088
F-N	1.361	1.348
N-N	1.241	1.233
F-N-N	112.14	110.38
N-N-N	147.94	156.18
F-N-N-N	135.9	135.2

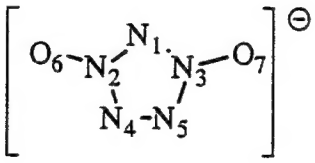
3



The DF optimization gave a planar C_{3h} structure. The MP2 optimization was constrained to C_{3h}.

	DF	MP2-FC
Energy	-518.28869	-517.01888
F-N	1.502	1.461
N-N	1.363	1.347
F-N-N	104.04	103.68

4



The DF optimization gave a planar C_{2v} structure. The MP2 optimization was constrained to C_{2v}.

	DF	MP2-FC
Energy	-424.07269	-423.02031
N1-N2	1.373	1.361
N2-N4	1.361	1.357
N4-N5	1.351	1.345
N-O	1.281	1.266
N2-N1-N3	101.72	101.83
N4-N2-N1	112.52	112.66
N5-N4-N2	106.62	106.42
O6-N2-N4	124.30	124.24
O6-N2-N1	123.18	123.10